

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0705-0188	
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE <b>000791-</b>	3. REPORT TYPE AND DATES COVERED Final Report <i>1 Jun 93 - 3 May 96</i>	
4. TITLE AND SUBTITLE <b>High Temperature Stability of Binary Microstructures Derived from Liquid Precursors.</b>			5. FUNDING NUMBERS <b>AFOSR AASERT F49620-93-1-0358</b>	
6. AUTHOR(S) <b>Fred F. Lange and A. D. Polli</b>			AFOSR-TR- <del>93</del> <i>97</i>	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Materials Department College of Engineering University of California Santa Barbara, CA 93106-5050</b>			<i>0105</i>	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) <del>Naval Air Station, Contracting Officer</del> <b>AFOSR/PC 110 Duncan Avenue, Suite B115 Bolling AFB DC 20332-0001</b>			10. SPONSORING/MONITORING AGENCY REPORT NUMBER <i>93-1-0358</i>	
11. SUPPLEMENTARY NOTES				
<div style="border: 1px solid black; padding: 5px; display: inline-block;"> <b>DISPOSITION STATEMENT R</b>  <b>Approved for public release</b>  <b>Distribution Unlimited</b> </div>				
12A. DISTRIBUTION/AVAILABILITY STATEMENT <i>unlimited</i>				
13. ABSTRACT (Maximum 200 words) <p>Chemical routes to synthesize inorganics start with solutions containing different metal-organic molecules that remain well mixed during evaporation to a solid precursor. The solid precursor decomposes and crystallizes during heating. Because decomposition (pyrolysis) occurs at very low temperatures relative to the melting temperature of the inorganic, a large free energy change exists for crystallization. This large free energy change is responsible for two very interesting phenomena. First, the size of the critical nucleus for spontaneous crystallization and growth is very small. Thus the grain size of the initial inorganic material produced during crystallization is <math>\leq 2</math> nanometers. Second, crystallization occurs at very low temperatures, i.e., either during or subsequent to pyrolysis. Thus diffusion is very limited, resulting in the crystallization of metastable phases, i.e., phases with unexpected (non-equilibrium) structures and/or phases with a solid-solution that is much greater than found for equilibrium conditions (high temperature heat treatments). With this understanding, nano-crystalline materials can be made that are very stable at high temperatures using the following procedure. The first step is to formulate a precursor composition that would produce at least two phases under equilibrium conditions. During and/or subsequent to pyrolysis, only one, metastable crystalline phase will form; it will have a nanometer grain size. Heating to higher temperatures where long range diffusion can occur will cause the single, metastable phase to partition to its stable phases. Since the second phase(s) partition with a smaller size than the initial metastable phase, a multi-phase composite is produced when the size of each phase can be <math>\leq 100</math> nano-meters. This nano composite can be stable at high temperatures because the growth of either phase requires long-range diffusion. These issues are detailed for three binary systems: t-ZrO<sub>2</sub>/c-ZrO<sub>2</sub>, ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>.</p>				
14. SUBJECT TERMS <b>HIGH TEMPERATURE, BINARY MICROSTRUCTURES, LIQUID PRESURSORS</b>			15. NUMBER OF PAGES <b>11</b>	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT <b>Unclassified</b>	18. SECURITY CLASSIFICATION OF THIS PAGE <b>Unclassified</b>	19. SECURITY CLASSIFICATION OF ABSTRACT <b>Unclassified</b>	20. LIMITATION OF ABSTRACT <i>U</i>	

**[DTIC QUALITY INSPECTED 8]**

**19970227 046**

# **High Temperature Stability of Binary Microstructures Derived from Liquid Precursors**

**Contract AFOSR/AASERT F49620-93-1-0358**

**Final Report**

**period: June 1, 1995-May 31, 1996**

**Due Date: July 31, 1996**

**From**

**Materials Department  
College of Engineering  
University of California  
Santa Barbara, CA 93106**

**Principal Investigator: Fred F. Lange**

**DTIC QUALITY INSPECTED 8**

## NANO-METER, BINARY COMPOSITES PRODUCED FROM LIQUID PRECURSORS VIA METASTABLE PHASES AND PHASE PARTITIONING

F. F. Lange and A. D. Polli

### Abstract

Chemical routes to synthesize inorganics start with solutions containing different metal-organic molecules that remain well mixed during evaporation to a solid precursor. The solid precursor decomposes and crystallizes during heating. Because decomposition (pyrolysis) occurs at very low temperatures relative to the melting temperature of the inorganic, a large free energy change exists for crystallization. This large free energy change is responsible for two very interesting phenomena. First, the size of the critical nucleus for spontaneous crystallization and growth is very small. Thus the grain size of the initial inorganic material produced during crystallization is  $\leq 2$  nanometers. Second, crystallization occurs at very low temperatures, i.e., either during or subsequent to pyrolysis. Thus diffusion is very limited, resulting in the crystallization of metastable phases, i.e., phases with unexpected (non-equilibrium) structures and/or phases with a solid-solution that is much greater than found for equilibrium conditions (high temperature heat treatments). With this understanding, nano-crystalline materials can be made that are very stable at high temperatures using the following procedure. The first step is to formulate a precursor composition that would produce at least two phases under equilibrium conditions. During and/or subsequent to pyrolysis, only one, metastable crystalline phase will form; it will have a nanometer grain size. Heating to higher temperatures where long range diffusion can occur will cause the single, metastable phase to partition to its stable phases. Since the second phase(s) partition with a smaller size than the initial metastable phase, a multi-phase composite is produced when the size of each phase can be  $\leq 100$  nano-meters. This nano composite can be stable at high temperatures because the growth of either phase requires long-range diffusion. These issues are detailed for three binary systems:  $t\text{-ZrO}_2/c\text{-ZrO}_2$ ,  $\text{ZrO}_2/\text{Al}_2\text{O}_3$ , and  $\text{ZrO}_2/\text{Fe}_2\text{O}_3$ .

## Introduction

Solution routes start with either aqueous or organic solutions containing precursor molecules for the different elements in the multi-element compound of interest. Provided the solution has the right rheology, it can be shaped into droplets, liquid jets, and thin films, which upon evaporation, make spherical particles, fibers, and either polycrystalline or single crystal [1] thin films on substrates, respectively. A variety of solution chemistries exist for multi-element compositions. These include metal organic molecules, [2-7] metal salts, [8] and polymers [9-11] that pyrolyze to synthesize oxides, carbides, and nitrides at modest temperatures (usually between 150 °C and 500 °C). Multi-element compounds can be synthesized by mixing similar precursor molecules in a common solvent prior to pyrolysis. 2-ethyl-hexanoates, suggested by Vest [5,6] for the processing of polycrystalline oxide films, are a specific metal carboxylate. These precursors cleanly pyrolyze to metal oxides and gaseous hydrocarbons, even in inert atmospheres. Metal acetates are another type of carboxylate with a much smaller hydrocarbon chain; they can dissolve in water. Metal carboxylates, such as 2-ethyl-hexanoates, do not bond together when mixed in solution. Other molecules like metal alkoxides react together when water is added to their common solvent to form networks (e.g., gels) composed of mostly -M-O-M- bonds with unreacted -OH and -OR 'fringes'. As shown in Fig. 1 these precursors can yield a higher weight fraction of inorganic material since they contain a much lower fraction of hydroxide and hydro-carbon groups, relative to other precursors such as the hexanoates. Other precursors form gels. 'Aluminum oxychloride', an aqueous solution of  $\text{AlCl}_3$  containing partially hydrolyzed  $\text{Al}^{+3}$  ions at pH 5, forms a gel when concentrated during evaporation. [8] Likewise, zirconium acetate species in aqueous solution also gel when concentrate. [7]

## Diffusion Limited Crystallization

The concept of kinetically limited crystallization simply states that if diffusion is severely limited during crystallization, a melt or glassy solid will crystallize to the lowest free energy crystalline structure for the given composition instead of seeking its lowest free energy state by partitioning into its stable assemblage of phases.

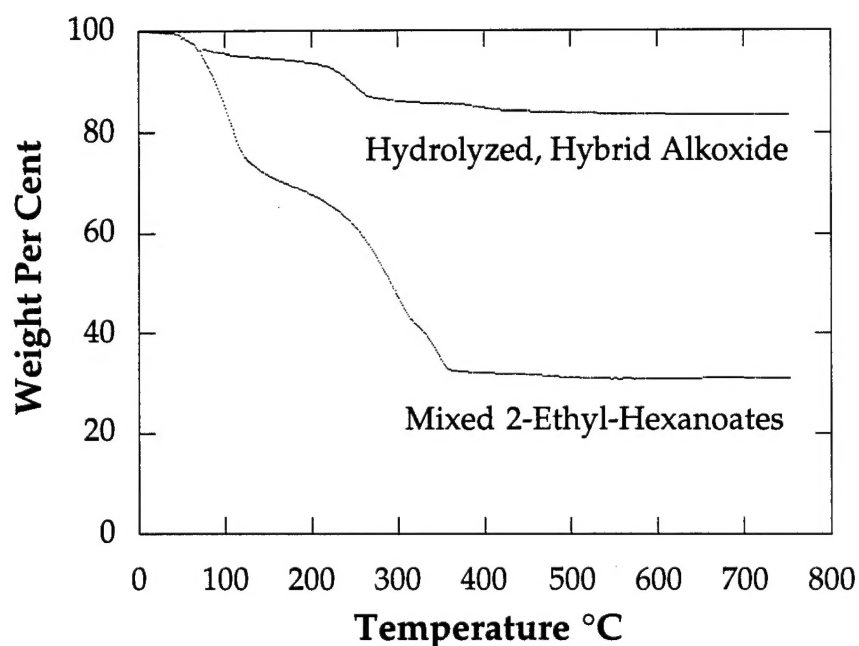


Figure 1. Thermogravimetric analysis of two precursors used to synthesize  $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ . [12]

The use of kinetically limited crystallization as applied to the low temperature crystallization of an arbitrary binary mixture of A and B. Figure 2a illustrates the equilibrium phase diagram for this hypothetical system, where A has the  $\alpha$  structure, B, the  $\beta$  structure, and the binary compound, AB, the  $\gamma$  structure. The first hypothetical experiment we perform is with composition a, which, we find, has crystallized as only one phase with the  $\alpha$  structure, but with lattice parameters different than usually reported for  $\alpha$ -A.

The free energy of the  $\alpha$ ,  $\beta$ , and  $\gamma$  structures as a function of composition at the temperature  $T_c$  is shown in Fig. 2b. Consistent with the equilibrium phase diagram, the lowest free energy compositions of  $\alpha$ ,  $\beta$ , and  $\gamma$  structures are compositions defined by A, B, and AB, respectively. We assume that the pyrolyzed precursor is in a 'glassy state' with some higher free energy also shown in Fig. 2b. With these assumptions, We see that if crystallization occurs without diffusion, composition a will crystallize as one phase with the  $\alpha$  structure and reduce its free energy by  $\Delta G_c$ . Because this structure also contains the element B in solid-solution, its lattice parameters are different than those reported for A. Further experiments with a wide range of precursor compositions produces the following results. For compositions between A and  $T_0$ , only the  $\alpha$  phase is formed; between  $T_0$  and b, only the  $\gamma$  phase, and between c and B, only the  $\beta$  phase is

found. For compositions between **b** and **c**, the pyrolyzed precursor does not crystallize until we heat to much higher temperatures. At lower temperatures the glassy state has the lowest free energy relative to either the  $\beta$  or  $\gamma$  phases, within this compositional region. In its simplistic form, this is the concept of kinetic limited crystallization.

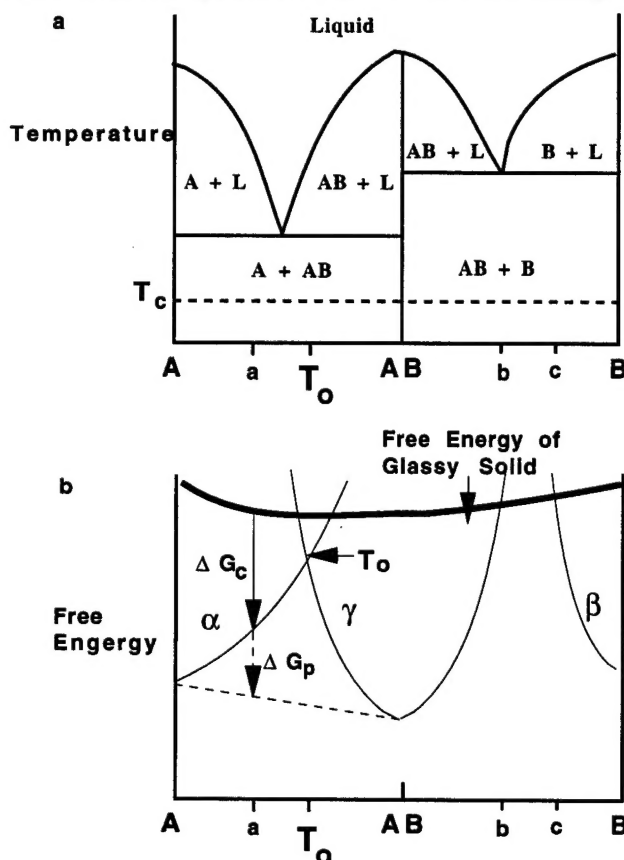


Figure 2 a) Hypothetical binary phase diagram, without minor solid-solution shown, b) and free energy vs composition at a temperature where crystallization occurs.

the beginning or segregated prior to kinetically limited crystallization, one might expect to crystallize two phases instead of one. More important, with this new understanding, we now discover a host of new processing techniques to develop and control unique microstructures.

Heating the metastable phase to higher temperatures where diffusion is no longer limited causes the elements to partition and develop a microstructures containing two (or more) phases. For example, x-ray diffraction analysis shows us that as we hold composition **a** at a high temperature, the lattice parameters of the  $\alpha$  structure slowly change to approach that reported for composition A. Concurrently, a new phase, AB, appears and increases its volume fraction. After some period of time, we can now explain

Experimentally one can determine the composition where both the  $\alpha$  and  $\gamma$  structures have the same free energy (defined as the  $T_o$  composition) and the lattice parameters of all three structures as a function of composition. Since we also recognize that  $\Delta G_c$  is a function of composition, we can also explain the systematic changes in the crystallization temperature of all three structures, e.g., the crystallization temperature increases as compositions approach  $T_o$  because the size of the critical nucleus increases ( $\Delta G_c$  decreases). Further, we recognize that in order to make these observations, the precursors must be mixed at the molecular level. That is, if the elements were not well mixed at

our phase assemblage using the equilibrium diagram, Fig. 2a. We also recognize that the driving potential for phase partitioning,  $\Delta G_p$ , not only depends on our initial, metastable composition derived through kinetic limited crystallization, but it also decreases as partitioning proceeds, i.e.,  $\Delta G_p$  decreases as the composition of the retained phase approaches its equilibrium composition.

### The $\text{ZrO}_2/\text{Gd}_2\text{O}_3$ Binary System [13]

Binary rare-earth, zirconia compositions fabricated by densifying powders, derived from precursor synthesized compositions, are dense, polycrystalline materials that exhibit high fracture toughness and strength due to a phenomena known as transformation toughening.

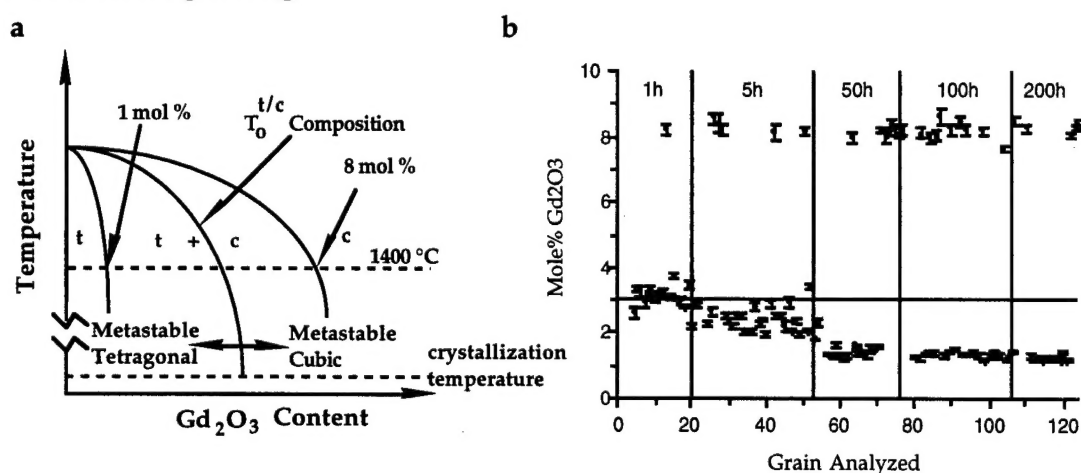


Figure 3 a) Schematic of  $\text{ZrO}_2$ -rich end of the  $\text{ZrO}_2$ - $\text{Gd}_2\text{O}_3$  binary phase diagram showing the two-phase (t=tetragonal, c=cubic) field and the  $T_0^{t/c}$  function. b) Grain by grain EDS analysis of  $\text{Gd}_2\text{O}_3$  content vs heat treatment time at 1400 °C for a composition containing 3 mole %  $\text{Gd}_2\text{O}_3$  crystallized at 450 °C from a Zr-acetate/Gd-nitrate precursor. [13]

Extensive studies in the  $\text{ZrO}_2$ - $\text{Gd}_2\text{O}_3$  binary system have shown that at 1400 °C, the maximum equilibrium solid-solubility of  $\text{Gd}_2\text{O}_3$  in tetragonal  $\text{ZrO}_2$  is  $1.0 \pm 0.1$  mol% and the minimum equilibrium solid-solubility in cubic  $\text{ZrO}_2$  is  $8.0 \pm 0.2$  mol% as shown in Fig. 3a which also shows the  $T_0^{t/c}$  composition as a function of temperature. This function is useful to predict what single, metastable phase is expected to crystallize during diffusion limited crystallization. At crystallization temperature for the Zr-acetate/Gd-nitrate precursors used to synthesize these materials ( $\approx 450$  °C), a metastable tetragonal phase crystallizes when the  $\text{Gd}_2\text{O}_3$  content is  $< 6.5$  mole %  $\text{Gd}_2\text{O}_3$  (all compositions to the left of the  $T_0^{t/c}$  curve), and a metastable cubic phase crystallizes when the  $\text{Gd}_2\text{O}_3$  content is greater (right side of the  $T_0^{t/c}$  curve).



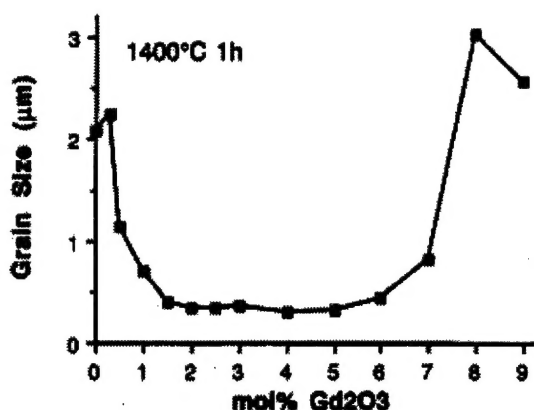


Figure 4 Grain size of  $\text{Zr}(\text{Gd})\text{O}_2$  as a function of  $\text{Gd}_2\text{O}_3$  content. Small grain size region is two phase field (see Fig. 3a) [13]

As shown in Fig. 3b complete partitioning of a metastable tetragonal phase containing 3 mole %  $\text{Gd}_2\text{O}_3$  requires  $> 200$  hr at  $1400^\circ\text{C}$ . During partitioning, cubic grains precipitate within the dense, polycrystalline metastable tetragonal material. These cubic grains constrain the growth of the tetragonal grains. Figure 4 shows that the grain size within the equilibrium two phase region (1 to 8 mole %  $\text{Gd}_2\text{O}_3$ ) is much smaller than the single phase fields ( $< 1$  mole %  $\text{Gd}_2\text{O}_3$ ,  $> 8$  mole %  $\text{Gd}_2\text{O}_3$ ).

The grain size is smallest when the cubic grains form a continuous, interpenetrating network (between 2 and 6 mole %  $\text{Gd}_2\text{O}_3$ ). For this range of composition, the growth of either tetragonal or cubic grains requires long range mass transport that can not be accomplished by grain boundary motion.

#### The $\text{ZrO}_2/\text{Al}_2\text{O}_3$ [14-16] and $\text{ZrO}_2/\text{Fe}_2\text{O}_3$ [17] Binary Systems

Aluminum oxide has one equilibrium structure,  $\alpha\text{-Al}_2\text{O}_3$  (corundum); it also has a number of metastable spinel-based structures which form readily when  $\text{Al}_2\text{O}_3$  crystallizes from precursors [18] or during melt quenching. [19-21] The size of the octahedral or tetrahedral sites in the  $\alpha\text{-Al}_2\text{O}_3$  structure are unfavorable for extensive  $\text{Zr}^{+4}$  occupancy, which severely limits the equilibrium  $\text{Al}_2\text{O}_3$  solubility in  $\text{ZrO}_2$  to  $\leq 2$  mole % at temperatures  $\leq 1400^\circ\text{C}$  as shown by the phase diagram determined by Alper and Stewart [22] and modified by Jayaram et al [19]. Crystallization via either rapid cooling [19] or heating after precursor pyrolysis [14,23] produces a single phase  $t\text{-ZrO}_2$  containing up to 40 mole %  $\text{Al}_2\text{O}_3$ . The crystallization temperature increases as shown in Fig. 5 ( $500^\circ\text{C}$  to  $900^\circ\text{C}$ ).

Compositions near the center of the binary crystallize at higher temperatures where diffusion is not kinetically constrained, and thus concurrently crystallize and partition to produce two metastable phases, viz.,  $t\text{-ZrO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$ , both with greatly extended solid-solubility. Thus at temperatures where structural units within the amorphous phase have sufficient mobility to 'snap' into place to allow a critical nucleus to spontaneously grow, the composition crystallizes as a single phase without partitioning with a free energy reduction, per unit volume, of  $\Delta G_c$ . As the composition 'moves away'



from the lowest free energy composition, the size of the critical nucleus for crystallization

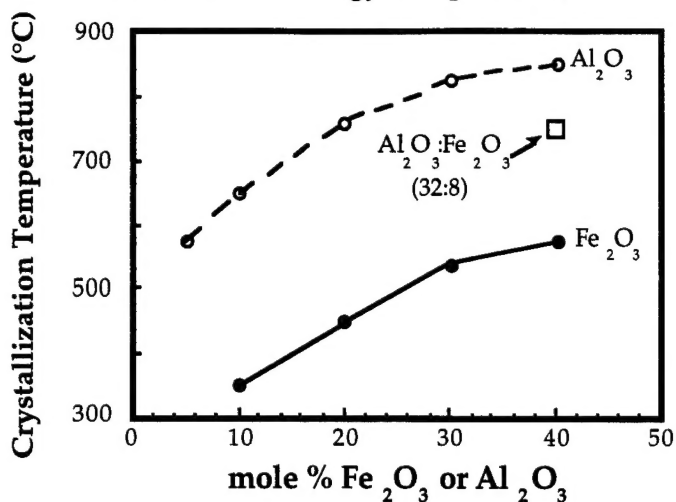
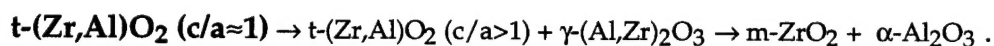


Figure 5 Crystallization temperature vs composition for ZrO<sub>2</sub>-rich compositions in the two binary systems. One ternary composition is shown. [14, 17]

increases because  $\Delta G_c$  decreases. Crystallization is thus delayed to higher temperatures where some long-range diffusion is required to form larger nuclei. When the composition is sufficiently different from the equilibrium compositions, the crystallization temperature can be too high to limit diffusion and prevent concurrent crystallization and phase partitioning. When compositions that produce single, metastable structures

during crystallization, are heated to temperatures where long-range diffusion is no longer kinetically limited, diffusion occurs, driven by the partitioning free energy,  $\Delta G_p$ , in an attempt to produce the equilibrium phase assemblage (m-ZrO<sub>2</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the temperature range considered). Because diffusion results in compositional gradients, a series of metastable phases with a range of solid-solution can be observed prior to observing the equilibrium phases. For the ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system, the observed partitioning sequence is [14]



The same sequence of crystallization, phase partitioning and transformation is observed for similar compositions in the ZrO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>, except each of these transitions occurs at a lower temperature as shown in Fig. 5. The same phenomena occur for the ternary composition, but at an intermediate temperature as shown in Fig. 5.

An example of another unique, nano-composite produced during phase partitioning is shown in Fig. 6 (top). It was produced [14] by first partitioning a metastable  $\text{Zr}_{(1-x)}\text{Al}_x\text{O}_{2-x/2}$  ( $x = 0.57$ ) into a  $t\text{-ZrO}_2 + \gamma\text{-Al}_2\text{O}_3$  at temperatures  $< 1200^\circ\text{C}$ , where grains of both phases are 50 to 100 nm in size. The  $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$  transformation within this two phase material initiates at  $\approx 1200^\circ\text{C}$ . [14-16] As shown, the  $\alpha\text{-Al}_2\text{O}_3$  grains grow as stacked plates. All plates within a given 'stack' have a common nucleus, and thus, a common crystallographic orientation. Because the two phases ( $t\text{-ZrO}_2 + \alpha\text{-Al}_2\text{O}_3$ ) are

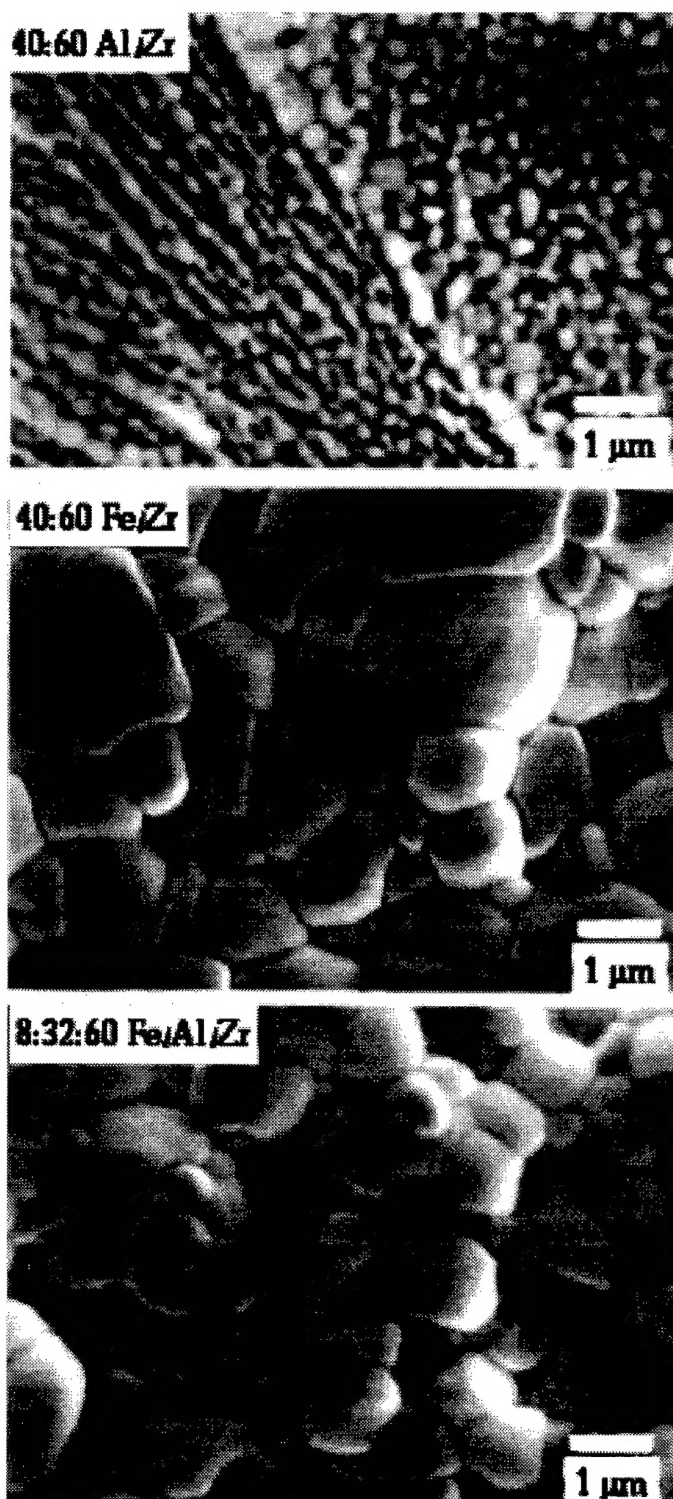


Figure 6. Comparison of the micrographs for the powders heat treated at the rate of 10°C/min to 1400°C for 1h for shown compositions. [17]

interpenetrating, and  $\alpha$ - $\text{Al}_2\text{O}_3$  exhibits relatively little diffusion at 1400 °C, this microstructure remains invariant for at least 100 hr at 1400 °C. [15] The reason why the microstructure forms a series of stacked plates is not fully understood, except for the fact that few  $\alpha$ - $\text{Al}_2\text{O}_3$  nuclei are formed during the transformation, and the transformation takes place as  $\text{ZrO}_2$  is excluded from the  $\gamma$ - $\text{Al}(\text{Zr})_2\text{O}_3$ . Thus, it is postulated that the plate like structure forms in the same manner as the eutectoid transformation of austenite. As shown in the middle micrograph of Fig. 6, the plate like microstructure does not occur for the same composition within the  $\text{ZrO}_2$ - $\text{Fe}_2\text{O}_3$ , where the  $\alpha$ - $\text{Fe}_2\text{O}_3$  nuclei per unit volume is much higher.[17] Instead, the final phase assemblage is two interpenetrating, polycrystalline materials,  $\text{ZrO}_2$  (light phase) and  $\alpha$ - $\text{Fe}_2\text{O}_3$ . The more refractory ternary composition (lower micrograph) produces a similar microstructure, but with a somewhat smaller grain size.

### Concluding Remarks

The synthesis of metastable phases with greatly extended solid-solutions is a natural phenomena for materials synthesized from precursors where elements are well mixed in the solution state. The concept of diffusion limited crystallization explains why these metastable phases form, and can be used to detail the sequence of other metastable phases that form during partitioning at higher temperatures where diffusion is no longer constrained. Because the metastable phase crystallizes as nano-meter crystallites and partitioned phases are of the same dimension, stable nano-composites can be formed via this processing route.

### Acknowledgment

Work leading to this review was sponsored by Contract AFOSR/AASERT F49620-93-1-0358

### References

- 1) F. F. Lange, *Science*, 273 [5277] 903-9 (1996)
- 2) J. Livage, M. Henry and C. Sanchez *Prog. Solid St. Chem.*, 18, 259-341 (1988).
- 3) C. J. Brinker and G. W. Scherer *Sol-Gel Science*, (Academic Press, NY 1990).
- 4) C. D. Chandler, C. Roger and M. J. Hampden-Smith *Chem. Rev.* 93, 1205-41 (1993).
- 5) R. W. Vest, in *Ceramic Films and Coatings*, J. B. Wachtman and R. A. Haber, ed. (Noyes Pub., Park Ridge, NJ, 1993) pp. 303-41.
- 6) J.V. Mantese, A.L. Micheli, A.H. Hamdi, and R.W. Vest, *MRS Bul.* 14, 48-53 (1989).
- 7) E. Leroy, C. Robin-Brosse, and T. P. Torre, in *Ultrastructure Processing of Ceramics, Glasses, and*

*Composites*. L. L. Hench and D. R. Ulrich, ed. (Wiley, NY, 1984) p. 219-31.

8) J.D. Birchall *Trans. J. Br. Ceram. Soc.*, 82, 153-45 (1983).

9) R.M. Laine and F. Babonneau *Chemistry of Materials* 5, 260-79 (1993).

10) J. Bill and F. Aldinger *Adv. Mater.* 7, 775-87 (1995)

11) Y. Saito, S. Koyama, Y. Sugahara, and K. Kuroda *J. Ceram. Soc. Japan* 104, 143-45 (1996).

12) A.D. Polli and F.F. Lange, *J. Am. Ceram. Soc.*, 78 [12] 3401-404 (1995).

13) D. K. Leung, C.-J. Chan, M. Rühle, and F. F. Lange, *J. Amer. Ceram. Soc.* 74 [11] 2786-92 (1991).

14) M.L. Balmer, F. F. Lange and C. G. Levi, *J. Am. Ceram. Soc.* 77 [8] 2069-75 (1994).

15) Mari Lou Balmer, F. F. Lange, V. Jayaram, and C. G. Levi, *J. Am. Ceram. Soc.* 78 [6] 14895-94 (1995).

16) Mari Lou Balmer, F. F. Lange, N. Das and H. Eckert, *J. Am. Ceram. Soc.* (in press)

17) Pravin K. Narwankar, F. F. Lange and Carlos G. Levi, Sent to *J. Am. Ceram. Soc.*

18) S. J. Wilson and J.D.C. McConnell, *J. Solid State Chem.*, 34, 315-22 (1980).

19) V. Jayaram, C.G. Levi and R. Mehrabian, *Materi. Sci. and Eng.*, A124, 65-81 (1990).

20) G. Kalonji, J. McKittrick, and L.W. Hobbs,; pp. 816-825 in *Advances in Ceramics*, Vol. 12, Science and Tech. of Zirconia II, Ed. by N. Claussen, M. Rühle, and A.H. Heuer. Am. Cer. Soc., Columbus, OH, 1981.

21) T. Ando and Y. Shiohara, *J. Am. Cer. Soc.* 74 [2] 410-17 (1991).

22) A.M. Alper, G.H. Stewart (ed.), *Science of Ceramics*, Vol.3, Academic Press, London, 1967, p. 339.

23) O. Yamaguchi, M. Shirai, and M. Yoshinaka, "Formation and Transformation of Cubic ZrO<sub>2</sub> Solid Solutions in the System ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>," *J. Am. Cer. Soc.*, 71[12] C-510-C-512 (1988).